PATENT SPECIFICATION 1,017,323

NO DRAWINGS.

1,017,323

Date of Application and filing Complete Specification: June 23, 1964. No. 25940/64.

Application made in United States of America (No. 290,154) on June 24, 1963.

Complete Specification Published: Jan. 19, 1966.

Index at Acceptance:—C1 A(E3B, E3X).

Int. Cl.:—C 01 f.

COMPLETE SPECIFICATION.

A Process for the Production of Sulphuryl Fluoride or Sulphuryl Chlorofluoride or both.

We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 61, Broadway, New York 6, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes for making sulphuryl fluoride, SO_2F_2, and/or sulphuryl chlorofluoride, SO_2ClF. Each is a known compound, and each is normally a colourless gas, their respective boiling points being about $-51°$ C. and $+7°$ C.

It has been proposed to make sulphuryl fluoride by reaction of elemental fluorine and sulphur dioxide, and by thermal decomposition of $Ba(FSO_3)_2$. Neither procedure has any commercial potentialities. It has also been proposed to make it by reaction of sulphur dioxide, chlorine, and hydrogen fluoride in the presence of a catalyst consisting of activated carbon alone at temperatures of 350—450° C. In this process, at the outset of an operation high yields of good quality sulphuryl fluoride are readily obtainable. However, evidently because of side reactions, the nature of which is not thoroughly understood, the activated carbon catalyst becomes poisoned rapidly; this brings several commercial disadvantages, the most important of which are, the notably short life of the catalysts, low weight recovery of sulphuryl fluoride per unit weight of catalyst used, and rapid dropping off of product yield and quality as poisoning of the activated carbon catalyst progresses. In catalytic operations in which catalyst poisoning is a derogating factor, poisoning can generally be decreased, and the catalyst life increased, by lowering the reaction temperature. However, investigations using activated carbon alone as catalyst and substantially lower temperatures of the order of 200—300° C., have shown that in this case the expected decrease in poisoning does not occur to any technically significant degree. These lower temperature operations were characterised by substantially the same deficiencies as the higher temperature processes, chiefly, short catalyst life and low sulphuryl fluoride recovery per unit weight of catalyst.

It has now been found that certain activated carbon-alkali metal bifluoride catalysts promote the conversion of sulphur dioxide to sulphuryl fluoride (presumably according to the equation $SO_2+Cl_2+2HF \longrightarrow SO_2F_2+2HCl$) to such an extent as to increase the life of the catalyst by fifty to several hundred percent, and to effect corresponding increases in sulphuryl fluoride production unit weight of catalyst. Moreover, it has been found that these catalysts enable temperatures considerably lower than the 350—450° C. of the prior art to be used.

Accordingly the invention comprises a process for the production of sulphuryl fluoride or sulphuryl chlorofluoride or both, which comprises effecting reaction between substantially anhydrous chlorine, sulphur dioxide and hydrogen fluoride at a temperature not exceeding 350° C. in the presence of a catalyst material comprising a major proportion by weight of active carbon and at least 5% by weight of an alkali metal bifluoride. (Unless otherwise stated, all proportions given throughout the specification are by weight.)

In one preferred method of carrying out the invention a substantially anhydrous gaseous

mixture consisting of chlorine, sulphur dioxide, and hydrogen fluoride, is fed into and through a reaction zone which contains activated carbon-alkali metal bifluoride catalyst material, while maintaining in the zone a temperature high enough to effect significant reaction but not above 350° C., discharging reaction products from the zone, and recovering sulphuryl fluoride from the products discharged.

The reactor and related accessories may be quite simple, and the sulphuryl fluoride may be recovered in accordance with conventional principles. The reactor and associated equipment, and the product recovery system, may for instance be along the lines described in the Examples.

The catalysts employed are preferably bodies of granular material consisting of activated carbon and alkali metal bifluoride. Any of the commercially available activated carbons may be used. Sizing may be in the range of 2 to 14 mesh (U.S. Standard Screen) (Openings from about 1.17 to 8 or 10 mm.). One example is Columbia grade CXC, mesh 6 to 8 (2—2.8 mm.), having a packed apparent density of about 0.45. Preferably however a higher density activated carbon is employed, a representative example being National Carbon JXC grade of mesh 6 to 8 and packed apparent density of about 0.63. The alkali metals include sodium, potassium, lithium, rubidium and caesium, and more usually sodium or potassium will be used; of these potassium is preferred, since potassium bifluoride has been found to give notably better results than sodium bifluoride.

The catalyst components may be associated in any suitable way, e.g. as layers in the reactor or as mechanical mixtures in which the alkali metal bifluoride is well dispersed throughout the activated carbon. However, the preferred catalysts are those in which the alkali metal bifluoride impregnates and is carried by the activated carbon. Usually the proportions of activated carbon and alkali metal bifluoride are chosen to give an alkali metal bifluoride content of 10—40%, preferably 10—30%, of the whole. These proportions apply regardless of whether the catalytic material is in layer form or a mechanical association or mixture of activated carbon and alkali metal bifluoride, or is in the form of activated carbon impregnated with and acting as a carrier for the bifluoride.

The catalyst material may be made by conventional procedures. For example, the quantity of alkali metal bifluoride to be used in making up of a batch of catalyst may be dissolved in enough water to permit thorough mixing of the resulting solution with the quantity of activated carbon to be employed, after which the water is evaporated off, and the resulting impregnated activated carbon dried by a known procedure. To thoroughly dry and otherwise condition the catalysts, the material after having been air dried to a moisture content below 0.2% and having been charged into a reactor, may be purged with an inert gas, e.g. nitrogen, at a temperature well above 100° C. e.g. about 150° C., for an hour or so prior to use.

The catalysts may be made in other ways. For example, activated carbon and the normal alkali metal fluoride may be charged into a reactor, and the normal fluoride converted to the bifluoride *in situ* by the action of hydrogen fluoride before the feed of the mixture of chlorine, sulphur dioxide and hydrogen fluoride is begun. Naturally the amount of alkali metal fluoride should be such as will yield the required amount of alkali metal bifluoride.

Experience shows that the bifluoride functions to a major extent by alternate release and replacement of hydrogen fluoride in for example KF.HF, and not as a major reactant. Thus it is found that the bifluoride is not used up in the reaction. Indeed in operations of the type illustrated in the Examples, the maximum charge of potassium bifluoride would be consumed in about an hour, if it were an important source of fluorine for the reaction. Further, in prior processes using activated carbon alone as catalyst, there is evidence that in some way or other sulphuric acid is formed in the reactor, and that this may be the major cause of poisoning the activated carbon and thus reducing its productive life. In the process of the invention, on the other hand, while it is thought that the bifluoride acts chiefly as a fluorine exchange catalyst, it seems possible that its presence in the reactor may result in the formation of an alkali metal sulphate which is much less poisonous to the catalyst than some side reaction products formed in the reactor when activated carbon alone is used as catalyst. Whatever the explanation may be, the overall results of the use of the new catalysts include a substantial increase in the life of the catalyst, and increased formation of sulphuryl fluoride per unit of catalyst employed.

As already indicated the reactants fed to the reactor will normally be chlorine, sulphur dioxide, and hydrogen fluoride, all substantially anhydrous. If desired however substantially anhydrous sulphuryl chloride may be used in place of part or all of the sulphur dioxide and chlorine, and unless specifically otherwise indicated, sulphuryl chloride is to be considered in what follows as the equivalent of the corresponding quantities of sulphur dioxide and chlorine.

The quantity of chlorine fed may be conveniently used as the basis for defining the relative proportions and rates of feed of the various reactants. The stoichiometric requirements are one mol each of chlorine and sulphur dioxide and two mols of hydrogen

fluoride. While any reasonably reactive proportions of chlorine, sulphur dioxide and hydrogen fluoride may be employed, an appreciable excess of chlorine may cause difficulties in the product recovery system and hence is not desirable. Preferably therefore when sulphuryl fluoride is to be the dominant product, at least one mol proportion of sulphur dioxide and at least two mol proportions of hydrogen fluoride are used per mol of chlorine. Ordinarily, a relatively small molecular excess of sulphur dioxide is most desirable, especially 1.05—1.5 mols per mol of chlorine though a larger excess may be employed. Similarly it is usually preferred to use 2.05—3.0 mols of hydrogen fluoride per mol of chlorine, though again a larger excess is permissible. Incoming chlorine, sulphur dioxide and hydrogen fluoride may be metered into a mixing manifold, and the resulting mixture charged into the reactor.

The temperature maintained in the reaction zone will depend on whether the main product is to be sulphuryl fluoride or sulphuryl chlorofluoride. However in either case it should be above 100° C. but not above 350° C. in order to avoid shortening the catalyst life and reducing the yield per unit of catalyst. To minimize possible borderline catalyst poisoning the maximum temperature is 325° C. When sulphuryl fluoride is required with the minimal amount of sulphuryl chlorofluoride, the temperature is preferably not lower than 150° C., and is preferably 175—325° C.

The contact time as in many catalytic processes, is highly variable depending upon other variable factors such as reaction temperature, catalyst composition and grain size, the product required, the type of apparatus, and the overall scale of operation. When maximum formation of sulphuryl fluoride with minimum formation of sulphuryl chlorofluoride is desired, the contact time will be longer than when the formation of appreciable amounts of sulphuryl chlorofluoride as a secondary product, and still more as the primary product, is desired. For any particular operation, apparatus and product desired, the determination of optimum values for the major process variables, such as temperature and contact time, is within the skill of the art, and may be done by test runs.

When sulphuryl chlorofluoride is to be the main product, small variations may be made in the reaction conditions described above. The chief changes are a reduction in the amount of hydrogen fluoride fed, a reduction in the reaction temperature, and possibly a decrease in the contact time. Stoichiometrically only half as much hydrogen fluoride is required, one mol of hydrogen fluoride per mol each of sulphur dioxide and chlorine. It is however still preferred to use an excess of sulphur dioxide and hydrogen fluoride, of the same relative degree as in making sulphuryl fluoride, i.e. 1.05—1.5 mols of sulphur dioxide, and 1.05 to 1.5 mols of hydrogen fluoride. The temperature will generally be 100—250° C., preferably 100—200° C. In order to avoid possible loss of sulphuryl chlorofluoride by hydrolysis, the material leaving the reactor may be introduced directly into a suitable still in which sulphuryl chlorofluoride is separated and recovered from other constituents, e.g. chlorine, sulphur dioxide, hydrogen chloride and fluoride, and sulphuryl fluoride by fractional distillation.

The pressure in the reaction zone may be superatmospheric if desired, though this has no particular advantage, except that a pressure of say 2—10 psig. may be used to cause the gas stream to flow through the apparatus train.

The following Examples illustrate the invention.

Example 1

In this run, the reactor employed comprised a bundle of 41 tubes, each about 4 metres long and having an internal diameter of about 5 cm. The bundle was mounted in a vertically elongated cylindrical casing providing a gas inlet manifold at the top ends of the tubes and a gas outlet manifold at the bottom ends. In turn, the casing was enveloped by a heating chamber associated with other equipment arranged to facilitate the maintenance of a desired temperature within the reactor.

The catalyst consisted of activated carbon (activated charcoal, grade National Carbon JXC, packed apparent density about 0.63, 6—8 mesh) impregnated with about 17% of potassium bifluoride (based on the total weight of the catalyst.) The reactor was charged with about 158 kg. of catalyst, of which about 26.75 kg. was potassium bifluoride.

A gaseous mixture of sulphur dioxide, chlorine and hydrogen fluoride (all anhydrous) was fed to the gas inlet manifold at the top end of the reactor, at a rate per hour of about 0.91 kg. mols of chlorine, 0.95 kg. mols of sulphur dioxide and 2.04 kg. mols of hydrogen fluoride. During a run of 87 hours, extraneous heat was applied to the reactor so as to maintain the temperatures within the reactor between about 290° C. at the upper end of the reactor, and about 190° C. at the bottom or gas outlet end.

The reactor exit gas, containing sulphuryl fluoride, hydrogen fluoride, hydrogen chloride, and smaller amounts of sulphuryl chlorofluoride, sulphur dioxide and chlorine, was passed through two series-connected water scrubbers which removed from the gas stream the hydrogen fluoride, hydrogen chloride, sulphur dioxide, chlorine, and most of the sulphuryl chlorofluoride. The gases leaving the

second water scrubber, containing sulphuryl fluoride with relatively small amounts of sulphuryl chlorofluoride and watei, were passed through a sulphuric acid scrubber to remove most of the moisture and finally dried by passing through a bed of activated alumina. The dried gas stream, containing sulphuryl fluoride and a small amount of sulphuryl chlorofluoride was compressed to 17.5—29.8 kg./cm², and the compressed gas was charged into a still operated to allow draw-off from the reflux of liquid sulphuryl fluoride, which was immediately packaged in a suitable container. The relatively small amount of sulphuryl chlorofluoride separated from the sulphuryl fluoride and was collected as still bottoms. During the 87 hour run, the hourly average rate of sulphuryl fluoride production, per 8 hour shift, was between a maximum of about 79 kg. and a minimum of 38.5 kg. per hour toward the end of the run. The average production overall was about 58.5 kg. per hour, and the total production was about 5093 kg. About 31.1 kg. of sulphuryl fluoride was recovered per kg. of catalyst material charged. The proportions of the chlorine, sulphur dioxide and hydrogen fluoride fed recovered as sulphuryl fluoride were respectively 63.4%, 60% and 56.4%.

EXAMPLE 2

The apparatus employed was the same as in Example 1. In this run, the reactor was charged with about 150 kg. of fresh catalyst of substantially the same composition as in Example 1; likewise the feeds of chlorine, sulphur dioxide, and hydrogen fluoride to the reactor, the reactor temperatures throughout the run, and the product recovery were substantially the same as in Example 1. Over a total run of about 86 hours, the average rate of sulphuryl fluoride production, per 8 hour shift, varied from a maximum of about 76 kg. per hour to a minimum of about 48.5 kg. per hour; the average for the run was about 57.6 kg. per hour, and the total sulphuryl fluoride production was about 4953 kg. About 33.1 kg. of sulphuryl fluoride was produced per kg. of catalyst charged. The proportions of the chlorine sulphur dioxide and hydrogen fluoride utilized were about 63%, 59% and 56.4% respectively.

EXAMPLE 3

The reactor of the previous Examples was charged with about 154 kg. of substantially the same catalyst as in the previous Examples, except that it contained about 23% by weight of potassium bifluoride, the balance being activated carbon. Kg. mols per hour feed of chlorine, sulphur dioxide, and hydrogen fluoride were respectively 0.86, 0.91 and 2.18. Throughout the run, which lasted about 80 hours, the temperature in the reactoi varied from about 250° C. at the upper end to about 190° C. at the bottom. The average rate of sulphuryl fluoride production, per 8 hour shift, was between a maximum of about 59 to a minimum of about 43.5 kg. per hour, an the total production of sulphuryl fluoride was about 3955 kg. About 25.6 kg./per kg. of sulphuryl fluoride was obtained of catalyst charged. The proportions of the chlorine, sulphur dioxide and hydrogen fluoride fed recovered as sulphuryl fluoride were about 55.5%, 54.1% and 45.1% respectively.

The following Table summarizes other similar operations. Parts are by weight.

Run No.	Duration of Run Hrs.	Carbon Type	% KFHF By Wt.	Total Catalyst Pts.	Feed Rate Chlorine Pt.Mols/hr.	Total Pts. SO_2F_2 Prod'n per run	Pts. SO_2F_2 Prod'n Per Pt. of Catalyst
1	100.5	JXC	17	Approx. 348	1—2	36,372 (Runs 1—3)	34.8 (Runs 1—3)
2	97	JXC	17	348	2		
3	81	JXC	17	348	2		
4	87	JXC	17	348	2	11,256	32.3
5	57	CXC	17	240	1.75—2	5,235	21.8
6	70.8	CXC	23	260	2	8,630	33.2
7	71.5	CXC	23	260	2	8,244	31.7

In Runs 1—4 the activated carbon used was the same as in Examples 1—3. In Runs 5—7, it was the lower density material previously described. In all of these runs, the temperatures were substantially as in Examples 1 and 2.

In a series of 73 tests, using about 270 parts of activated carbon alone as catalyst, temperatures substantially in the range of 190° to 320° C., and other procedural factors about the same as above described, production of sulphuryl fluoride made per test run was about 2,470 parts, about 9.2 parts of sulphuryl fluoride were made per part of catalyst, and the service life of the catalyst for comparative purposes was taken as 100%. Corresponding values for Runs 1—3 of the above Table were about 12,124 parts, about 34.8 parts, and about 490%.

WHAT WE CLAIM IS:—

1. Process for the production of sulphuryl fluoride or sulphuryl chlorofluoride or both, which comprises effecting reaction between substantially anhydrous chlorine, sulphur dioxide and hydrogen fluoride at a temperature not exceeding 350° C. in the presence of a catalyst material comprising a major proportion by weight of active carbon and at least 5% by weight of an alkali metal bifluoride.

2. Process according to claim 1, wherein the catalyst material comprises 10—40% by weight of the alkali metal bifluoride.

3. Process according to claim 1 or 2, wherein the catalyst material comprises potassium bifluoride.

4. Process according to any one of the preceding claims, wherein the alkali metal bifluoride is formed *in situ* from the corresponding alkali metal fluoride and hydrogen fluoride before the feed mixture of chlorine, sulphur dioxide and hydrogen fluoride is introduced.

5. Process according to any one of the preceding claims, wherein the catalyst material is obtained by impregnating grains of the active carbon with an aqueous solution of the alkali metal bifluoride or fluoride, and evaporating off the water.

6. Process for the production of sulphuryl fluoride according to any one of the preceding claims, wherein for each mol proportion of chlorine there is employed 1.05—1.5 mol proportion of sulphur dioxide and 2.05—3.0 mol proportions of hydrogen fluoride.

7. Process according to claim 6, wherein the reaction is carried out at a temperature of 175°—325° C.

8. Process for the production of sulphuryl chlorofluoride according to any one of claims 1—5, wherein for each mol proportion of chlorine there is employed 1.05—1.5 mol proportion of sulphur dioxide and 1.05—1.5 mol proportions of hydrogen fluoride.

9. Process according to claim 8, wherein the reaction is carried out at a temperature of 100° C.—200° C.

10. A modification of the process of any one of the preceding claims, in which part at least of the chlorine and sulphur dioxide are replaced by the equivalent amount of substantially anhydrous sulphuryl chloride.

11. Process for the production of sulphuryl fluoride or sulphuryl chlorofluoride or both according to claim 1 substantially as hereinbefore described.

12. Sulphuryl fluoride and sulphuryl chlorofluoride obtained by a process claimed in any one of claims 1—11.

J. A. KEMP & CO.,
Chartered Patent Agent,
14 South Square,
Gray's Inn, London, W.C.1.

Abingdon: Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1966.
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.